



Volatile Losses from Resuspended Dredged Material

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PURPOSE: This technical note describes laboratory investigations conducted to obtain flux data for the emission of volatile organic chemicals (VOCs) from sediment resuspended in the water column. Data obtained from these investigations are being used to evaluate and validate previously developed air emission conceptual models (Valsaraj et al. 1997a). Laboratory experimental techniques and results obtained during these investigations are described. In addition, a model addressing the multi-media (including air) chemical fate of polyaromatic hydrocarbons during dredging operations is presented.

BACKGROUND: Contaminated sediments and dredged materials are potential sources of volatile compound emissions. These emissions can occur during both dredging operations and after placement in a confined disposal facility (CDF). During dredging, a portion of the sediment is released into the water column where contaminants in the sediment can be desorbed and become available for volatilization to the air above the water column.

Thibodeaux (1989) and Valsaraj et al. (1995) discuss four major locales where volatile emissions may occur during dredging and disposal of contaminated sediments:

- Sediment exposed to air during transport, disposal, and following dewatering at the disposal site.
- Resuspension of sediment in the water column as a result of mechanical disturbance.
- Ponded sediment, after placement and prior to dewatering.
- Vegetated covered sediment.

Locales 1 through 3 are the main sources of concern involving emissions of VOCs from contaminated sediments. Earlier investigations conducted under the Long Term Effects of Dredging Operations Program focused on emissions from exposed material (Price et al. 1997, 1998, 1999; Valsaraj et al. 1997a, 1999; Ravikrishna et al. 1998). At present, extensive field monitoring data for emissions during dredging operations do not exist. In the case of this report, information on specific emissions from resuspended sediment is needed in order to evaluate and verify predictive equations addressing chemical release to water and subsequent volatilization of the chemicals from the water column to air during dredging operations.

INTRODUCTION: Dredging and disposal operations result in increased suspended solids concentrations at both the dredging site and during active disposal of material into a CDF. At present, the data are insufficient to evaluate volatile emissions under differing sediment

resuspension conditions. The collection of this data will enable investigators to assess possible volatile contaminant exposure levels and to evaluate and validate predictive equations and models addressing volatile emissions during dredging operations.

Previous investigations focusing on the redistribution of contaminants into the water column as a result of sediment resuspension have been conducted at Louisiana State University (Valsaraj et al. 1997b). Laboratory experiments have been conducted investigating the effects of differing suspended solids concentrations on polyaromatic hydrocarbon (PAH) emissions from Indiana Harbor Canal (IHC) sediment, to develop and evaluate mathematical models addressing VOC emissions during dredging.

MATERIALS AND METHODS:

Sediment. Sediment from IHC was used in all laboratory experiments. This sediment was used due to existing laboratory and field data on volatile emissions from exposed sediment (Price et al. 1999; Valsaraj et al. 1999). Sediment physical and chemical properties are presented in Table 1.

| Table 1 Physical and Chemical Properties of Indiana Harbor Canal Sediment | |
|--|--------------------------------------|
| Property | Value |
| Moisture content (%) | 49.00 |
| Percent sand | 45.00 |
| Percent silt | 46.00 |
| Percent clay | 8.00 |
| Percent total organic carbon | 6.90 |
| Percent oil and grease | 0.94 |
| Bulk density, g/cm ³ | 0.60 |
| Compound | Sediment Concentration, mg/kg |
| 2-Methylnaphthalene | 11.40 |
| Naphthalene | 38.30 |
| Acenaphthylene | 1.54 |
| Acenaphthene | 26.80 |
| Fluorene | 18.00 |
| Phenanthrene | 51.00 |
| Anthracene | 10.70 |
| Fluoranthene | 50.70 |
| Pyrene | 59.20 |
| Chrysene | 40.30 |
| Benzo(a)Anthracene | 26.50 |
| Benzo(b)Fluoranthene | 19.40 |
| Benzo(k)Fluoranthene | 14.00 |
| Benzo(a)Pyrene | 21.70 |
| Indeno(1,2,3-C,D)Pyrene | 14.70 |
| Dibenzo(A,H)Anthracene | 0.98 |
| Benzo(G,H,I)Perylene | 15.70 |
| Total Recoverable Hydrocarbons | 12,790.00 |
| Arochlor 1248 | 4.10 |

Flux Chamber. Volatile emissions were measured using an apparatus designed at LSU (Figure 1). The chamber, a cube 50 cm on each side, was constructed of 3/8-in. plexiglass. The moveable “mixing” grid consisted of an 8 x 8 mesh made of 1.27-cm square aluminum bars with a bar length of 49 cm. The grid was connected to a variable-speed DC motor by a stainless steel shaft, which when attached to a programmable controller, could maintain oscillation frequencies from 60 to 600 rpm. The grid stroke length could be varied from 2 to 12 cm. The chamber lid was sealed with a gasket to produce an airtight fit and fitted with numerous ports to allow for addition of sediment, air supply, exit port, and temperature measurements. Water samples could be taken from ports on the side of the chamber.

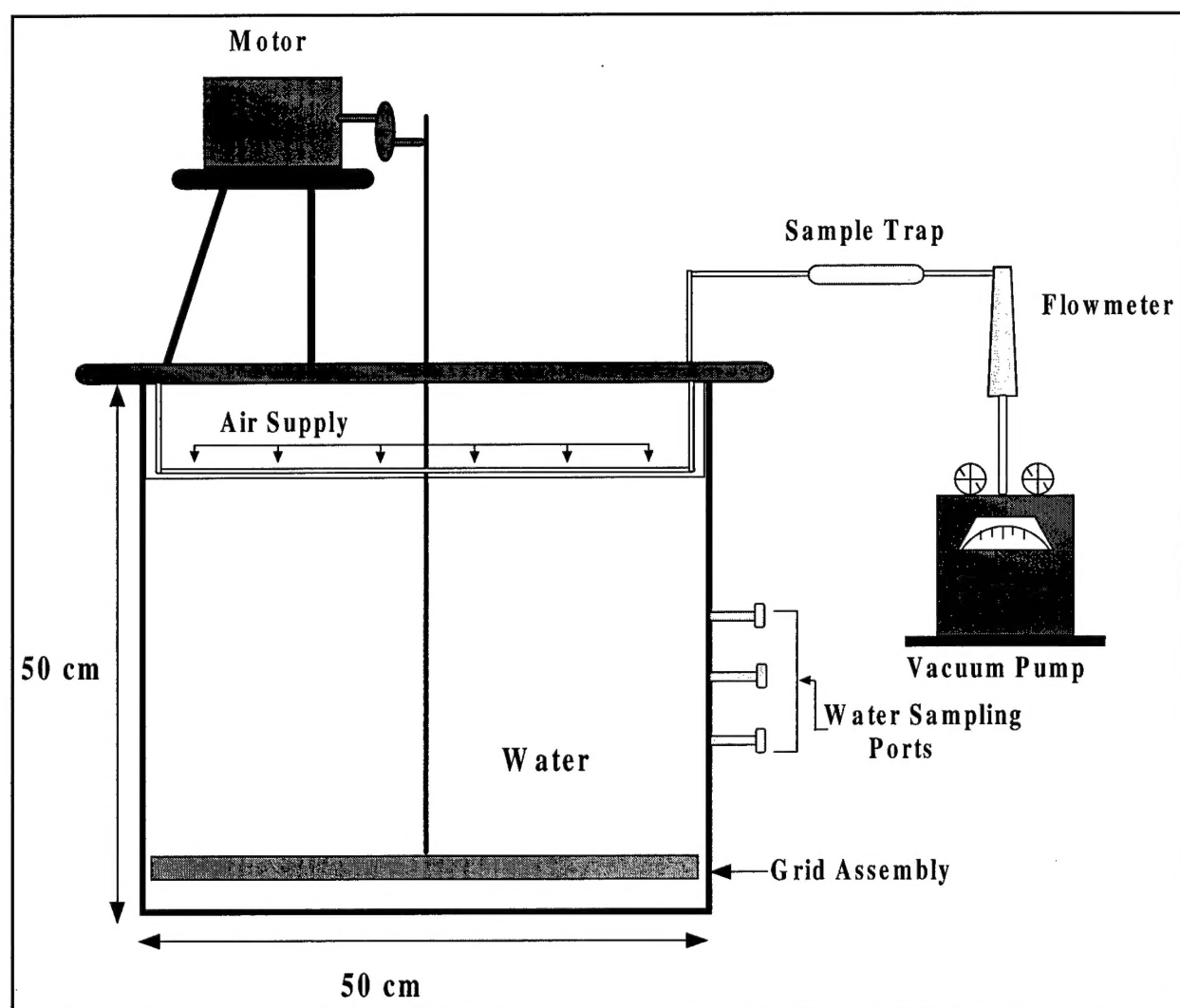


Figure 1. Sediment resuspension chamber experimental schematic

Experimental Design. The flux chamber was filled to a depth of 37 cm (92 L) with water. Varying amounts of sediment and different oscillation speeds were tested to determine the amount of sediment and speed necessary to maintain suspended solids concentrations in the water column. Three suspended solids concentrations were selected for testing for volatile

emissions and included low (100 mg/L), medium (400 mg/L), and high solids (2,900 mg/L) concentrations.

Three separate experiments were conducted at the three suspended solids concentrations. The chamber was filled with water to a depth of 37 cm. Oscillation of the grid (275 rpm) was started prior to addition of sediment. The amount of sediment to produce the desired suspended solids concentration was then added and the suspended solids were allowed to stabilize in the water column for a 30-min period. Sampling was conducted over a period of 6 days.

Air samples. Prior to initiation of sampling for air emissions, the overlying air in the chamber was flushed by pulling air over the surface of the water for 15 min at 12 L/min (2.7-min residence flushing time). This air flow was maintained for the duration of each experiment at each suspended solids concentration. A contaminant-specific air sampling trap containing 2 grams of XAD-2 resin (Supelco, Inc.) was then attached to the chamber exit port and air was pulled through the trap for a 2-hr period while oscillation was maintained. After 2 hr the trap was removed and oscillation was stopped. This sample was to simulate contaminant emissions during dredging when suspended solids are at the highest at each TSS concentration. Air sampling then consisted of one continuous run with samples being pulled 2, 6, 24, 48, 72 and 144 hr after mixing was stopped. These samples were to simulate contaminant emissions after dredging is stopped and suspended solids begin to settle. Traps were removed at the end of each sampling interval and solvent was extracted and analyzed according to EPA method 8270 (U.S. Environmental Protection Agency (USEPA) 1982).

Contaminant flux through the chamber $N(t)$ was calculated using the equation

$$N(t) = \frac{\Delta m}{\Delta t A_c}$$

where

Δm = mass (ng) of compound collected on trap in time Δt (hr)

A_c = area of the sediment-air interface, cm^2

Water samples. Water samples for total suspended solids (TSS) concentrations were taken at the start and end of the initial 2-hr sample and then at the end of each air sampling interval. TSS concentrations were determined according to EPA Method 148-A (USEPA 1982).

RESULTS:

Total Suspended Solids (TSS). Suspended solids concentrations remained relatively steady during the initial 2-hr sample interval (during grid oscillation) in each TSS test. Table 2 gives TSS concentrations over time for each test.

Contaminant Fluxes. During dredging and filling operations associated with a CDF, a portion of the sediment is released into the water column. Contaminants can then be desorbed from the sediment particles into the water. The extent of desorption determines the availability

Table 2
Total Suspended Solids Concentrations Over Time

| Sample Time, hr | 100 mg/L | 400 mg/L | 2900 mg/L |
|-----------------|----------|----------|-----------|
| 2 | 100 | 415 | 2910 |
| 4 | 30 | 270 | 1230 |
| 21 | 30 | 140 | 820 |
| 46 | 10 | 100 | 490 |
| 70 | 10 | 60 | 510 |
| 142 | 10 | 40 | 390 |
| 356 | 0 | 30 | 140 |

of compounds in the aqueous phase for volatilization. Volatilization from the water occurs across the air-water interface and from there, the chemical enters the atmosphere. The tendency of a chemical to volatilize is generally related to the chemicals' Henry's Constant. Henry's Constant is defined as the equilibrium distribution of a volatile compound between air and water and is related to the compound's aqueous solubility, vapor pressure, and molecular weight. Compounds with a high Henry's Constant will tend to accumulate in the air whereas those with a lower Henry's constant will tend to prefer water.

Contaminant fluxes increased with increasing suspended sediment concentrations, increasing Henry's Constant, and decreasing sediment water partition constant ($\log K_{oc}$). Table 3 gives contaminant properties for all compounds analyzed. The PAHs detected in the exit air traps included naphthalene, 2-methylnaphthalene, acenaphthene, acenaphthylene, fluorene, phenanthrene, anthracene, fluoranthene, and pyrene. For a comparison, Figure 2 shows initial fluxes of naphthalene (NAPHTH), acenaphthene (ACENAP), and phenanthrene (PHENAN), which have varying solubilities, $\log K_{oc}$, and Henry's Constants. Sediment loading concentrations of these three compounds were 38.3, 26.8, and 51 mg/kg, respectively. Regardless of sediment loading, desorption of these compounds from the solids and volatilization from the water column were governed by the individual compounds' chemical properties. This behavior was seen for all PAH compounds analyzed in these studies (i.e., contaminant emissions decreased with decreasing Henry's Constant, and decreasing chemical solubility). Fluxes over time for these three compounds are compared in Figure 3. Fluxes decreased rapidly after oscillation was stopped and sediment solids were allowed to settle. Naphthalene fluxes decreased to 0.03 ng/cm²/hr 72 hr after the mixing grid was shut off in all three tests (Figure 3a). Emissions of acenaphthene decreased to 0.01, 0.03, and 0.3 ng/cm²/hr in the 100-, 400-, and 2900-mg/L tests, respectively, in the same time period (Figure 3b). Acenaphthylene and 2-methylnaphthalene showed similar trends. 2-methylnaphthalene fluxes fell below 0.03 mg/L in all three tests 72 hr after oscillation was stopped and acenaphthylene fluxes fell below 0.3 ng/cm²/hr in the same time period. Phenanthrene fluxes showed a different trend by increasing to a peak emission rate 4 hr after oscillation was stopped, followed by a decrease in emissions to 0.008, 0.02, and 0.15 ng/cm²/hr by the 72-hr sampling interval (Figure 3c). Anthracene emissions also followed this trend in the 400- and 2900-mg/L tests with fluxes being below 0.05 ng/cm²/hr 7 days after mixing was stopped. In comparison, fluoranthene and pyrene, which have much lower solubilities and Henry's Constants (Table 3),

Table 3
Contaminant Properties

| Compound | Solubility, mg/L | Vapor Pressure, Pa@25°C | Log K _{oc} , L/kg | Henry's Constant, PA m ³ /mol |
|-------------------------|------------------|-------------------------|----------------------------|--|
| Naphthalene | 31.2 | 10.4 | 2.97 | 48.9 |
| 2-Methylnaphthalene | 25.4 | 9.07 | 3.40 | 41.02 |
| Acenaphthene | 3.93 | 0.307 | 3.79 | 24.42 |
| Acenaphthylene | 3.93 | 0.893 | 3.75 | 11.5 |
| Fluorene | 1.90 | 0.793 | 4.15 | 10.13 |
| Anthracene | .075 | 7.8 x 10 ⁻⁴ | 4.20 | 6.59 |
| Phenanthrene | 1.29 | .0263 | 4.36 | 3.981 |
| Pyrene | 0.135 | 8.9 x 10 ⁻⁴ | 4.92 | 1.20 |
| Fluoranthene | 0.260 | 1.24 x 10 ⁻³ | 4.74 | 0.659 |
| Chrysene | 0.002 | 5.7 x 10 ⁻⁷ | 6.90 | 0.45 |
| Benzo(a)Anthracene | 0.010 | 1.47 x 10 ⁻⁵ | 6.30 | 0.101 |
| Benzo(b)Fluoranthene | 0.014 | 6.67 x 10 ⁻⁵ | 5.70 | 0.054 |
| Benzo(k)Fluoranthene | 0.0008 | 4.93 x 10 ⁻⁶ | 5.99 | 0.111 |
| Benzo(a)Pyrene | 0.0043 | 2.53 x 10 ⁻⁵ | 6.26 | 0.009 |
| Indeno(1,2,3-C,D)Pyrene | na | na | na | na |
| Dibenzo(A,H)Anthracene | 0.0005 | 3.7 x 10 ⁻¹⁰ | 6.22 | 0.0076 |
| Benzo(G,H,I)Perylene | 0.00026 | 1.39 x 10 ⁻⁸ | 6.20 | 0.015 |
| Arochlor 1248 | 0.054 | 0.066 | 5.44 | 50 |

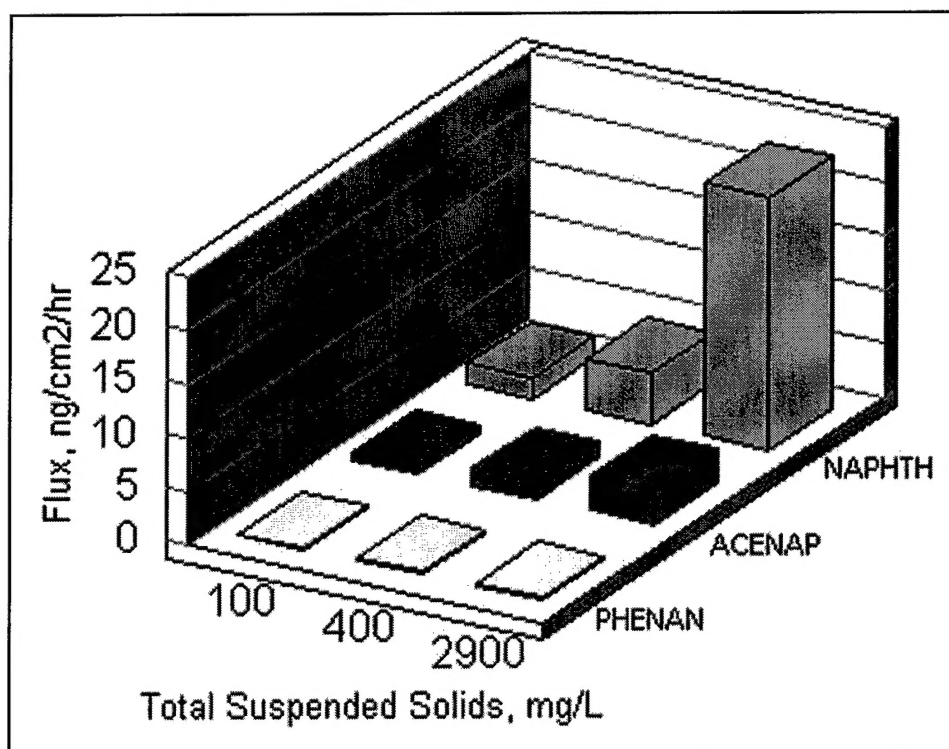


Figure 2. Comparison of initial PAH fluxes at each suspended solids concentration

exhibited a different flux trend. Peak emissions did not occur until 48 hr after oscillation was stopped (Figure 4).

Aqueous Concentrations. Aqueous contaminant concentrations correlated to TSS concentrations and fluxes seen in the 100-mg/L and 400-mg/L tests. Concentrations decreased over time in conjunction with decreasing suspended solids and contaminant emissions. Figure 5 shows aqueous concentration over time for naphthylene, acenapthene, and phenanthrene. At the higher suspended solids concentration, aqueous concentrations increased before decreasing at the 48-hr sampling period. This behavior correlated with emissions for a majority of the hydrocarbon compounds.

Extrapolation of these laboratory experiments suggests that in a CDF, air emissions will be greatest during dredging and disposal. However, the operation is more like a steady-state scenario (rather than a transient one), so that conditions of resuspension are maintained thereby maintaining volatilization at a high level as well. After cessation of dredging and disposal operations, resuspended material would settle and the concentrations of contaminants available for volatilization from the water column would decrease substantially. A steady-state model is needed to extend the laboratory investigations to field conditions.

Model Development. A multimedia model for assessing contaminant fate during dredging operations has been developed by personnel at Louisiana State University (Sanchez, Thibodeaux, and Valsaraj 2000). The model was developed by performing a series of steady-state mass balances around a box containing the dredged element and surrounding water plus sediment as illustrated in Figure 6. The model consists of a dredge element that initiates chemical release in a

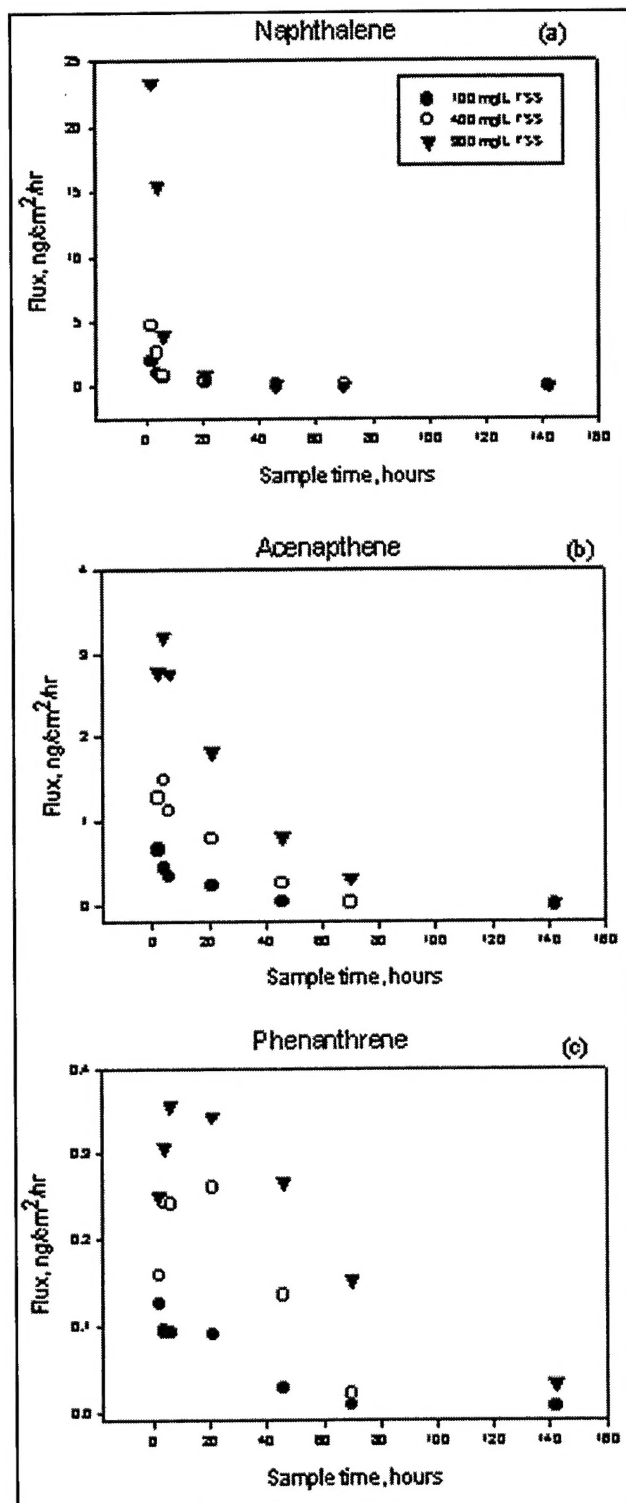


Figure 3. Comparison of PAH fluxes over time at each suspended solids concentration

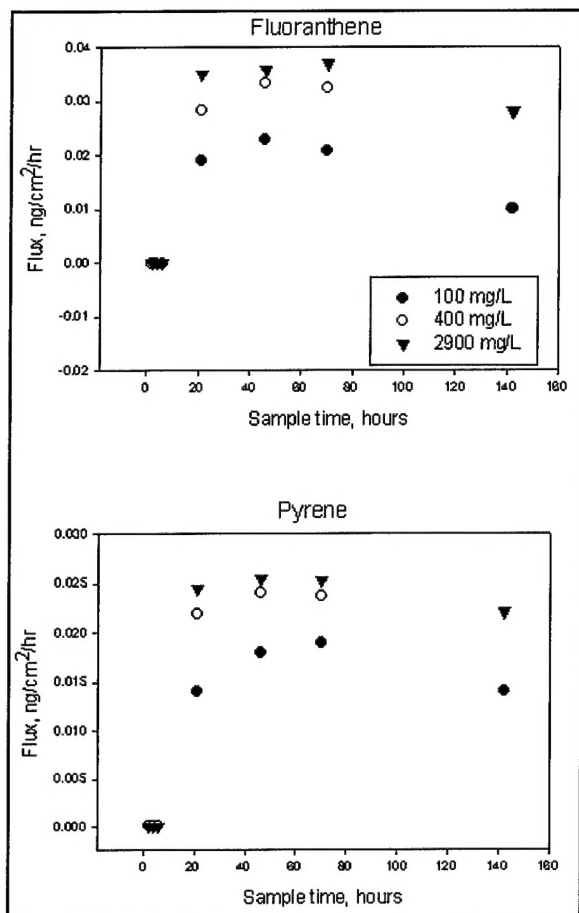


Figure 4. Comparison of fluoranthene and pyrene fluxes over time at each suspended solids concentration

flowing stream and gives an algorithm for contaminant transport to air, water and sediment, both with and without silt curtain containments. The model quantifies these losses as fractions and contains mass balance output for the original in-place contaminant quantity, which is targeted for dredging, and the quantity "delivered to shore" (a measure of dredging operation efficiency). Contaminant losses due to advection, volatilization, and settled material (dredged suspended sediment deposits (DSSD)) can be calculated.

This model was developed at LSU using data gained when studying the effectiveness of dredging at three sites: Bayou Bonfouca, Slidell, LA.; Grasse River, Massena, N.Y.; and Manistique Harbor, Manistique, MI. Model development and application to the Bayou Bonfouca site are described in Sanchez, Thibodeaux, and Valsaraj (2000), who found that the model successfully

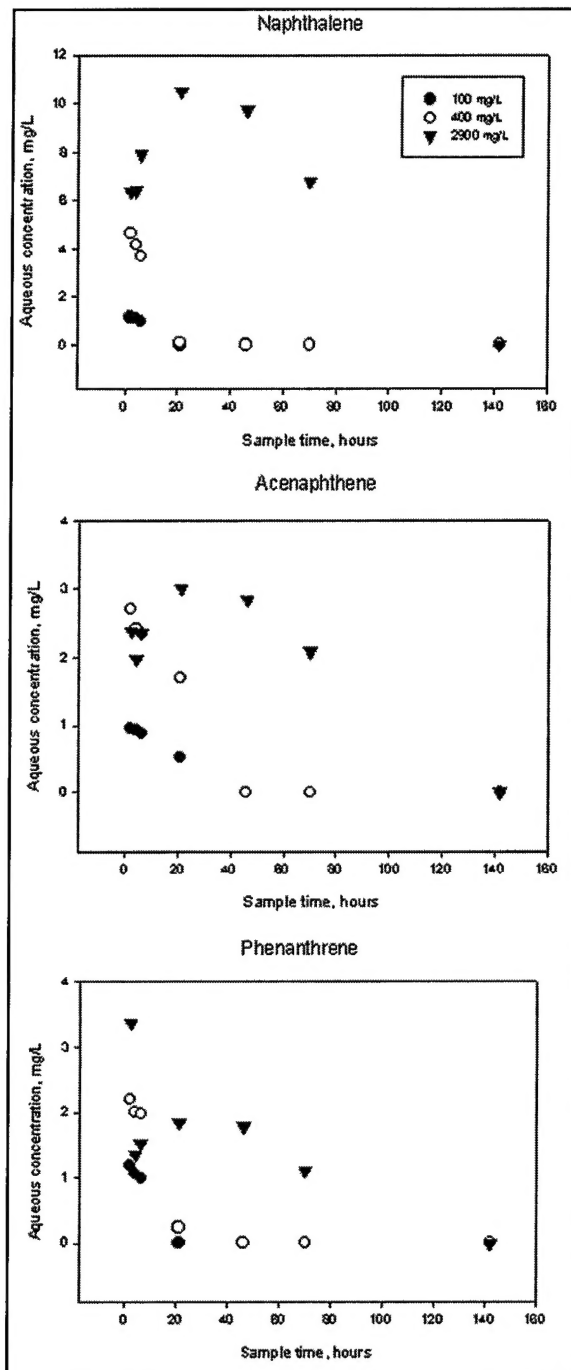


Figure 5. Aqueous PAH concentrations over time at each TSS concentration

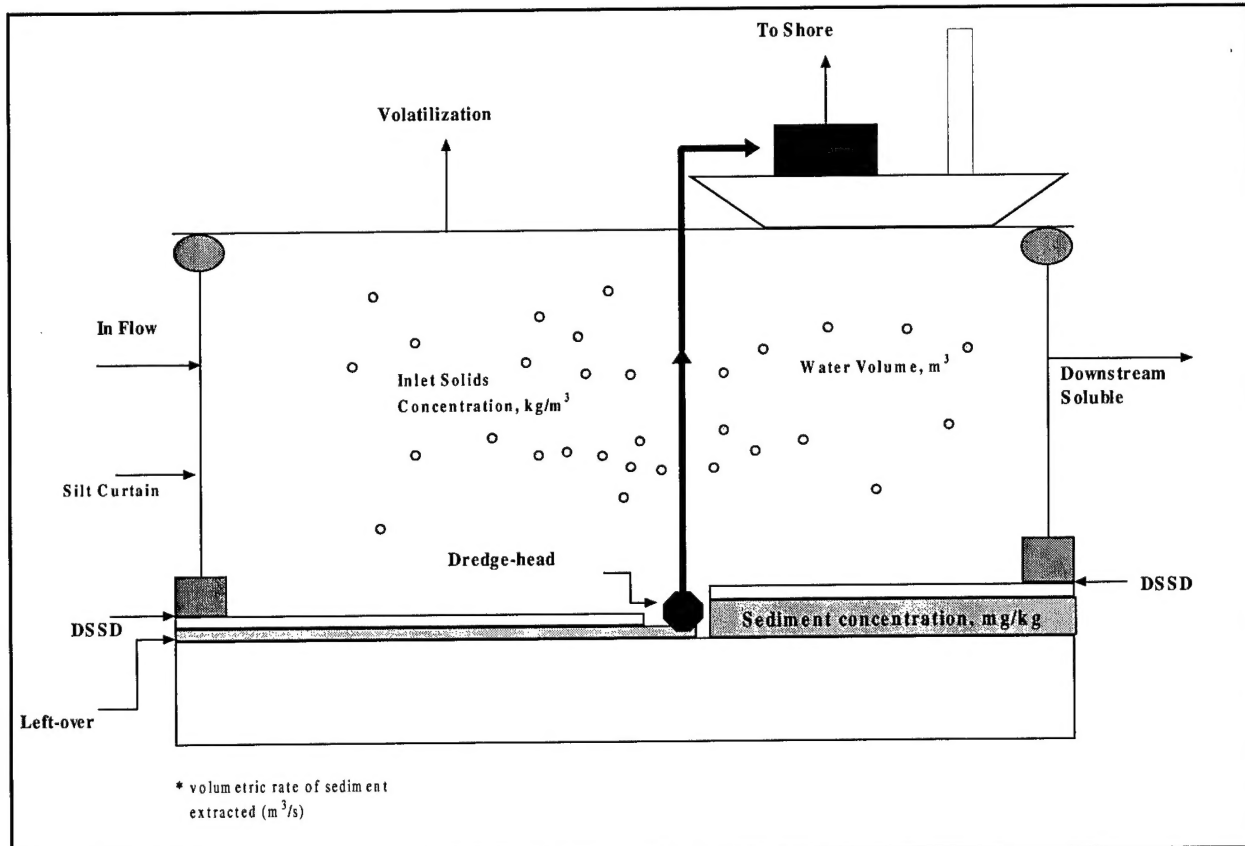


Figure 6. Possible pathways for fate of dredged contaminated sediment

quantified contaminant losses due to advection, volatilization, and DSSD for both 0 and 100 percent efficient silt curtain containment. In addition, the overall mass balance was calculated, which allowed estimation of the amount of contaminant delivered to shore. The one parameter that was varied during comparative model simulation was a parameter referred to as a Turbidity Generating Unit (TGU), which is used to define the solids mass suspended per unit volume of material extracted. This is a measure of the turbidity generated by the dredge; and therefore, the higher the TGU, the higher the amount of chemical resuspended. Chemical resuspension in turn leads to dispersion of contaminants to all phases (air, water, and sediment). The dredge operates within a volume of water, V_w (m^3), with continuous flow through the box, Q (m^3/s). A solids mass balance, in kilograms per second, is given by:

$$\rho_{32}^{\circ} * Q + TGU * V_R = \rho_{32} * Q \quad (1)$$

where

ρ_{32}° = inlet solids concentrations in solution (kilograms per cubic meter)

V_R = volumetric rate of sediment extracted (cubic meters per second)

The chemical balance is developed as follows. Before dredging, the sediment bed has a chemical concentration ω_c° (milligrams per kilogram). After dredging commences, particles become suspended and equilibrium is established between the particle-bound chemical (ω_c) and

the chemical in solution (ρ_{c2}). This equilibrium is given by a partition coefficient of chemical between solids and water K_{A32} (liters per kilogram). At equilibrium $K_{A32} = \omega_c / \rho_{c2}$ the chemical balance performed around the box in milligrams per second is:

$$\begin{aligned} &(\rho_{32}^\circ * \omega_c^\circ * Q) + (\rho_{c2}^\circ * Q) + (TGU * V_R * \omega_c^\circ) = \\ &(TGU * V_R * \omega_c) + (\rho_{c2} * Q) + {}^1K_{AC2} * (\rho_{c2} - \rho_{c1}^*) * A_D \end{aligned} \quad (2)$$

where

ω_c° = inlet concentration of chemical in particles

A_D = dredging area

The left-hand side of Equation 2 represents the inflow terms: inlet flow of chemical on particles, inlet flow of chemical in solution, and generation of chemical-laden particles from the sediment-bed by the dredge. The right-hand side represents the outflow terms: flow of chemical on suspended particles, outlet flow of chemical in solution, and evaporation. The evaporation term consists of an overall mass transfer coefficient ${}^1K_{AC2}$ and a driving force term $(\rho_{c2} - \rho_{c1}^*)$ where ρ_{c1}^* is the concentration of chemical in air in equilibrium with water. This equilibrium between air and water is assumed to follow Henry's law ($\rho_{c1} = H_c * \rho_{c2}^*$).

These equations are the working forms of the steady-state multimedia model with Equation 1 being used to estimate the suspended solids concentration and Equation 2 used to estimate the chemical concentration generated by the dredging operation.

Table 4 compares model output of contaminant losses (total PAHs) in open-water disposal using two different TGU values. In order to compare overall losses through each separate media, it is important to quantify the total amount of chemical present prior to dredging (total in place). Other loss media calculated and presented in Table 4 include that volatilized, and that carried through advection (the movement of a chemical downstream through flow). The chemical can be carried downstream either in solution (soluble form) or on particles. From these modeling efforts it can be seen that an increase in TGU value results in a substantial increase in the amount of contaminant released or lost through volatilization, and through advection.

Table 4
Multimedia Model Output Comparison Between Two TGU Values, Totals in kg

| Pathway | TGU = 17.6 kg/m ³ | TGU = 55.8 kg/m ³ |
|---------------------------------|------------------------------|------------------------------|
| Total Contaminant Mass in Place | 785667.2 | 785667.2 |
| Volatilization | 3684.7 | 10128.7 |
| Advection (particles) | 2041.2 | 9924.2 |
| Advection (soluble) | 2041.4 | 4546.0 |
| Contaminant Mass to Shore | 730424.8 | 713593.2 |

The model described herein has been developed to assess chemical fate during dredging and to quantify contaminant losses due to advection (both soluble and particulate), volatilization, and sediment redeposited back to the sediment bed for two types of silt curtain containment. The model is currently being further developed and refined at LSU. Data generated during laboratory investigations described herein and laboratory investigations being conducted at LSU are being used to test and validate model predictions. Upon validation, the model will be incorporated into the Automated Dredging and Disposal Alternatives Modeling System (ADDAMS) suite of models currently available through the Waterways Experiment Station at: <http://www.wes.army.milel/elmodels/index.html#addams>.

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REFERENCES

- Price, C., Brannon, J., Myers, T., Valsaraj, K. T., Thibodeaux, L., and Reible, D. (1997). "Development of laboratory procedures to predict volatile losses from exposed sediments," *Environmental Effects of Dredging Technical Note EEDP-02-23*, U.S. Army Engineer Research and Development Center, Vicksburg, MS.
- Price, C., Brannon, J., Yost, S., Ravikrishna, R., and Valsaraj, K. T. (1999). "Prediction of volatile losses from contaminated exposed sediments," *Environmental Effects of Dredging Technical Note EEDP-02-28*, U.S. Army Engineer Research and Development Center, Vicksburg, MS.
- Price, C., Brannon, J., Yost, S., Valsaraj, K. T., and Ravikrishna, R. (1998). "Volatile losses from exposed sediment," *Environmental Effects of Dredging Technical Note EEDP-02-24*, U.S. Army Engineer Research and Development Center, Vicksburg, MS.
- Ravikrishna, R., Valsaraj, K. T., Yost, S., Price, C. B., and Brannon, J. M. (1998). "Air emissions from exposed, contaminated sediment and dredged materials 2. Diffusion from laboratory-spiked and aged field sediments," *Journal of Hazardous Materials* (60), 89-104.
- Sanchez, F., Thibodeaux, L. J., and Valsaraj, K. T. (2000). "A multimedia model for assessing chemical fate during environmental dredging," Interim Report. Gordon A. and Mary Cain Department of Chemical Engineering, Louisiana State University, Baton Rouge, LA.
- Thibodeaux, L. J. (1989). "Theoretical models for evaluation of volatile emissions to air during dredged material disposal with applications to New Bedford Harbor, Massachusetts," Miscellaneous Paper EL-89-3, U.S. Army Engineer Waterways Experiment Station, Vicksburg, MS.
- U.S. Environmental Protection Agency. (1982). "Test methods for evaluating solid waste physical and chemical methods," SW-846, 2d ed., National Technical Information Service, Springfield, VA (NTIS No. PB87-120291).
- Valsaraj, K. T., Choy, B., Ravikrishna, R., Thibodeaux, L. J., Reible, D. D., Price, C., Brannon, J. M., and Myers, T. (1997b). "Air emissions from contaminated sediments and dredged materials; 1. Experimental data in laboratory microcosms and mathematical modeling," *Journal of Hazardous Materials* (60), 65-87.
- Valsaraj, K. T., Ravikrishna, R., Choy, B., Reible, D. D., Thibodeaux, L. J., Price, C. B., Yost, S., Brannon, J. M., and Myers, T. E. (1999). "Air emissions from exposed contaminated sediments and dredged material," *Environmental Science and Technology* (33), 142-149.

- Valsaraj, K. T., Ravikrishna, R., Orlins, J. J., Smith, J. S., Gulliver, J. S. Reible, D. D., and Thibodeaux, L. J. (1997a). "Sediment-to-air mass transfer of semi-volatile contaminants due to sediment resuspension in water," *Advance in Environmental Research* 1 (2), 145-156.
- Valsaraj, K. T., Thibodeaux, L. J., Reible, D. D. (1995). "Dredging, remediation and containment of contaminated sediments," ASTM STP 1293, K. R. Demars; G. N. Richardson; R. N. Yong; and R. C. Chaney, eds., American Society for Testing and Materials, Philadelphia, 227-238.

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